Removal of phenol from water using fenchol-menthol hydrophobic deep eutectic solvent

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Abstract. Hydrophobic deep eutectic solvents (HDESs) are regarded as a potential green alternative to conventional organic solvents in separation processes such as liquid-liquid extraction, due to their favourable properties, such as lower vapour pressure and tunable properties. The present work investigated the application of HDES which is synthesised from fenchol and menthol, in the removal of phenol from water. The HDES was synthesised experimentally at a fenchol mole fraction range of 0.1 to 0.9. The experimental results showed that stable liquidus HDES was successfully formed when the fenchol mole fraction in the HDES was 0.2 – 0.9. Further investigation showed that HDES with a fenchol mole fraction of 0.2, which had a low viscosity and high stability in water, had the highest phenol removal efficiency. The phenol removal process was highly sensitive to solution pH and solution-to-HDES ratio. In contrast, phenol removal was less affected by initial concentration and temperature. A high phenol removal efficiency of up to 95.9% was achieved in this study, which further showed the positive feasibility of HDES to serve as an alternative to conventional organic solvents in the liquid-liquid extraction of phenol from water.

1 Introduction

Phenol (C_6H_5OH) is an aromatic compound that is characterised by a hydroxyl group attached to a carbon atom of a benzene ring. It exhibits significant toxicity owing to its capacity to permeate cellular membranes and induces protein denaturation. Phenol exhibits a high degree of absorption when exposed through various pathways (oral, dermal contact, inhalation) and it rapidly disperses throughout the body [1]. In humans, phenol specifically targets the central

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nervous system, giving both acute and chronic adverse effects such as respiratory arrest, abrupt weight loss, vertigo, and anorexia [2]. Adverse health conditions such as diarrhoea, mouth sores, were also reported at an intake level of 10 – 240 mg of phenol [3]. Due to its high toxicity, a strict limit is imposed on the level of phenol permitted in industrial effluent. In Malaysia, the Department of Environment prescribes phenol limits ranging from 0.001 to 1 mg/L, depending on the discharge location. Nevertheless, the removal of phenol from industrial effluent is challenging, as the phenol concentration is often high enough to cause adverse health effects, but too low to be recovered [4].

Liquid-liquid extraction remains one of the common separation processes for phenol removal whereby phenol is extracted from wastewater using a solvent. An extraction efficiency of up to 99.8% is reported to be achievable for phenol when a formulation containing tributylphosphane-diethyl carbonate-cyclohexane at a 2:2:6 ratio is used as the solvent [5]. However, it is noteworthy that the use of toxic and hazardous organic solvents such as methyl isobutyl ketone, and methyl propyl ketone remains a substantial drawback in the liquid-liquid extraction systems [6].

The discovery of hydrophobic deep eutectic solvents (HDESs) in 2015 is a significant milestone, as the HDES displayed good stability in water due to its hydrophobic nature. HDESs also typically have lower viscosities than hydrophilic DES, making them suitable to be used as solvent in water treatment applications [7]. Recently, HDESs have been identified as a potentially safer substitute for the toxic solvents utilised in liquid-liquid extraction processes. Works involving the use of HDES as a substitute for the liquid-liquid extraction of pollutants from water, such as bisphenol A [8], and chlorophenols [7] have been reported. On the removal of phenol from aqueous environments using HDESs, some works reported using HDESs synthesised from organic acids with alcohols [9] and trioctylphosphine oxide and menthol [10] with good removal efficiencies. Nevertheless, it is noteworthy that the research on the use of HDESs for the removal of phenol is still scarce. Therefore, the present work investigated the application of HDES that were synthesised using fenchol and menthol as novel solvent in the removal of phenol from water using liquid-liquid extraction. The effect of different parameters, such as HDES components mole fraction, pH, solution-to-HDES ratio, initial concentration and temperature on phenol removal using HDES was evaluated.

2 Materials and methods

2.1 Materials

Phenol (99.5%, AR) and menthol (99%, CP) were acquired from R&M Chemicals, while fenchol (≥ 96%, FG) was purchased from Sigma-Aldrich. The chemicals were used without additional purification. Solutions of sodium hydroxide and hydrochloric acid were made by dissolving sodium hydroxide pellets (R&M Chemicals, AR) and diluting concentrated hydrochloric acid (Merck Millipore, 37 %) with distilled water, respectively. Distilled water was used in preparation of all solutions in this study.

2.2 Experiments

2.2.1 Synthesis of HDES and characterisation study

In this study, fenchol (FEN) was used as the hydrogen bond donor (HBD) and menthol (MEN) was used as the hydrogen bond acceptor (HBA) [11]. The HDESs were prepared by mixing FEN and MEN at different FEN mole fractions, ranging from 0.1 – 0.9 in glass scintillation vials. The vials were then placed into a water bath, and the contents were heated up to a temperature of 60°C. The mixture was stirred at a stirring speed of 600 rpm until a clear, homogeneous liquid was obtained. The HDES was left passive cooling to room temperature and the physical appearance of the HDES was observed. The melting point and viscosity of the HDES were determined using Mettler Toledo DSC 3 STARe system and Anton Paar GmBH MCR 301 rheometer, respectively. Fourier Transform Infrared Spectroscopy (FTIR) was used to evaluate the formation of HDES, with a Thermo Scientific Nicolet iS10 spectrometer.

2.2.2 Liquid-liquid extraction

A volume of 1 mL of synthesised HDES was contacted with 10 mL of 1000 mg/L phenol-contaminated water in scintillation vials. The mixture was homogenised at 600 rpm for 30 minutes and was left idle for phase separation after the experiments. Then, the aqueous phase was taken using a syringe to minimise disturbance to the phase interface. Phenol concentration in the aqueous sample was determined using a UV-visible spectrophotometer at a wavelength of 270 nm after diluting the aqueous samples using diluted acid solution by a dilution factor of 10.

2.2.3 Analytical methods

The removal efficiency of phenol from the aqueous phase (*RE*) and phenol uptake into the HDES phase (C_{HDES}), were calculated using Equations (1) and (2):

$$RE(\%) = \frac{C_0 - C_f}{C_0} \times 100 \tag{1}$$

$$C_{HDES}(\mathrm{mg/mL}) = \left(\frac{C_0 - C_f}{1000}\right)\left(\frac{V_{aq}}{V_{HDES}}\right) \tag{2}$$

where
C_0: initial phenol concentration in aqueous phase (mg/L); C_f: final phenol concentration in aqueous phase (mg/L); V_{aq}: volume of phenol solution used in the experiment (mL); V_{HDES}: volume of HDES used in the experiment (mL)

3 Results and discussion

3.1 Synthesis and screening of HDES

HDES formation was observed between FEN and MEN at all FEN mole fractions (0.1 to 0.9, denoted as DES1 – DES9) at the synthesis conditions, which is in agreement with Fan *et al* [11]. However, it was noted that the HDES synthesised at 0.1 FEN mole fraction (DES1) solidified upon passive cooling to ambient room temperature, which demonstrates that the melting point of the HDES is higher than ambient room temperature. In contrast, other HDES remained in liquid phase for at least 24 hours. Water miscibility tests were further carried out for these HDES. It was observed that the HDES were stable in forming two immiscible layers with water for at least 24 hours.

The capability of these HDES in removing phenol from aqueous solution was further investigated. Fig. **1** shows that a removal efficiency of > 60% was obtained by the HDES. The molar ratios between the HBD and HBA have been recognised to be a significant factor in determining the physical and chemical properties, as well as the selectivity for a particular solute to the HDES [12].

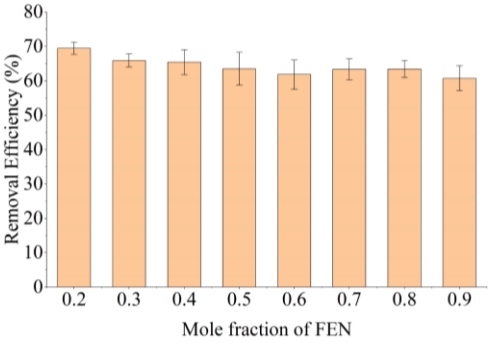

Fig. 1. Effect of mole fraction of FEN in HDES on phenol removal efficiency.

In this study, the mole fractions of FEN in the HDES were found to affect the removal efficiency, in which lower FEN mole fraction gave better removal efficiency. Therefore, the HDES synthesised at 0.2 FEN mole fraction (DES2), which attained the highest removal efficiency was selected for further study.

3.2 Characterisation study

The formation of DES2 was identified using FTIR and DSC analysis. Fig. **2** shows the comparison of FTIR spectra between DES2 and its parent materials. Typically, alcohol functional groups have a characteristic infrared absorption frequency of 3200 – 3600 cm^{-1}. This is further exemplified by the O-H absorption peaks acquired for alcohol-based starting materials FEN (3401 cm^{-1}) and MEN (3244 cm^{-1}). After the synthesis, the absorption peak for alcohol functional group in DES2 was shifted to 3337 cm^{-1}, which indicated the formation of hydrogen bonding between FEN and MEN [13]. This could be further validated by the analysis of melting point of the mixture by DSC, of which the melting point of DES2 was determined to be 8.1°C. The depression in the melting point further indicated the formation of hydrogen bonds in the eutectic mixture. In addition, the viscosity of DES2 at a temperature range of 20 – 50 °C was determined to have a range of 8.9 – 83.3 mPa·s, which fulfils the criteria of < 100 mPa·s to be classified as a low-viscosity solvent [13].

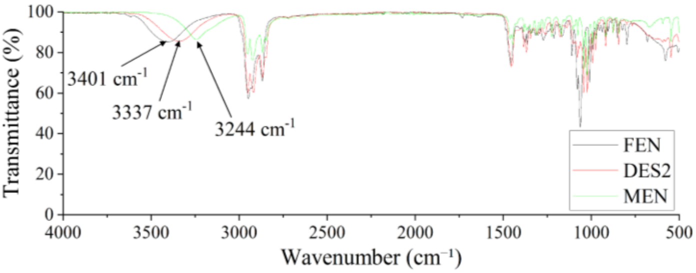

Fig. 2. FTIR spectra for FEN, MEN, and DES2.

3.3 Effects of operating parameters

The effect of different parameters, namely: pH, solution-to-HDES ratio, initial concentration of phenol, and temperature on the removal efficiency of phenol was investigated.

Figure 3(a) shows that the removal efficiency has less variation when the solution is at acidic to neutral conditions (pH 3 – 7). However, a small decrease in the removal efficiency was observed when the pH was 9, and the decrement became drastic when the pH was further elevated to 11. This could be due to the fact that pH is highly affecting the ionisation state of phenol species and consequently affecting the selectivity during the extraction [14]. Phenol is a weak acid and has a pK_a value of 9.98 [15]. The dissociation of phenol to phenoxide ion will be predominant at a pH of higher than 9.98, while the molecular form will be predominant at a pH of lower than 9.98. Based on the results, it was found that DES2 was capable of extracting molecular phenol via hydrogen bonding, but not phenoxide ion. It was deduced that the drastic decrease in removal efficiency at pH 11 can be attributed to the fact that the predominant form of phenol is phenoxide ion, which may have disrupted the formation of hydrogen bond interactions. The trends are in line with others' works that show a sharp reduction in the removal efficiency of phenolic compounds when pH was raised to 10 [16] and the optimum pH for removal was attained at pH < 7 [17].

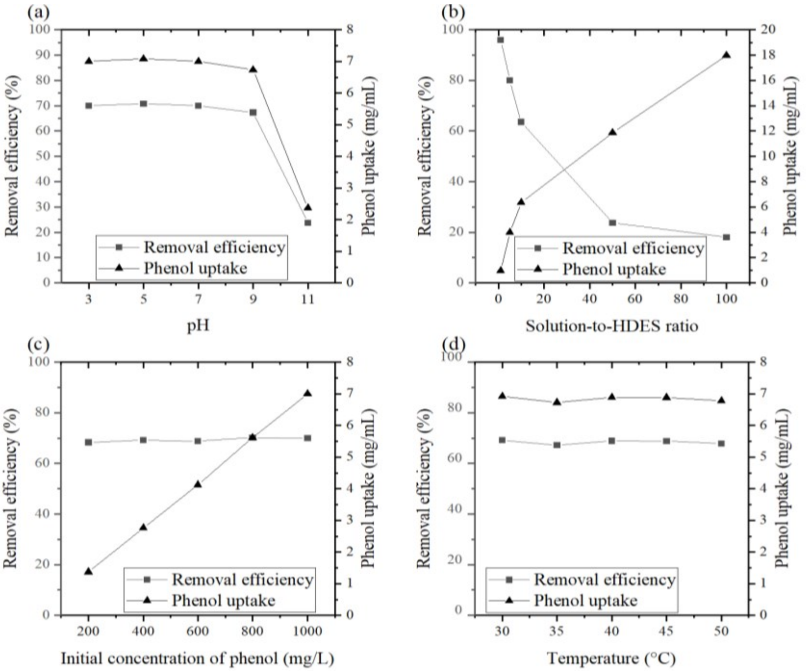

Fig. 3. Effect of operating parameters on phenol removal efficiency and phenol uptake by DES2: (a) pH, (b) solution-to-HDES ratio, (c) initial concentration of phenol, (d) temperature (Constant parameters: extraction time = 30 min; stirring speed = 600 rpm; initial concentration of phenol = 1000 mg/L; pH = 6.6, ratio of phenol solution to HDES = 10:1, temperature = ambient.).

Figure 3(b) shows that the removal efficiency decreases when increasing the solution-to-HDES ratio from 1 to 100. An excellent phenol removal efficiency of 95.9% was achieved at a solution-to-HDES ratio of 1. The results are also in agreement with Cheng *et al* [18], who achieved a phenol removal efficiency of around 93% at a solution-to-HDES ratio of 1 with HDES synthesised from menthol and nonanoic acid. At high solution-to-HDES ratios, there was insufficient amount of HDES to ensure effective contact between the HDES and phenol solution, resulting in low phenol removal efficiency. Nevertheless, it was worth noting that phenol uptake was increased from 0.96 mg/mL to 18.0 mg/mL as the solution-to-HDES ratio was increased from 1 to 100, indicating that DES2 had a high capacity to uptake phenol from water. The results as shown in Figure 3(c) suggest that there is no significant effect on phenol removal efficiency when the initial phenol concentration is increased from 200 mg/L to 1000 mg/L. This effect might be explained by the degree of phenol solvation being similar at the concentrations tested [9]. The results were similar to those obtained by Sas *et al*. as it was observed that the removal efficiency of phenol using ionic liquids was almost independent of the initial concentration of phenol [19]. This suggested that the HDES were capable of removing phenol in a wide range of concentrations from aqueous environments. The phenol uptake was found to increase from 1.37 mg/mL to 7.00 mg/mL when the phenol concentration was increased from 200 to 1000 mg/L. The experimental results as shown in Figure 3(d) show that phenol extraction by DES2 was independent of temperature ranging from 30°C – 50°C. The observations might be attributed to the fact that equilibrium extraction was achieved at a relatively short extraction time within 30 minutes.

4 Conclusions

The application of HDES as solvent in phenol removal from water was investigated. HDES was successfully synthesised using fenchol and menthol. The synthesised HDES were capable of removing phenol from water, in which the HDES with FEN mole fraction of 0.2 (DES2) gave highest phenol removal efficiency. Phenol removal by DES2 was found to be higher at low to neutral pH and low solution-to-HDES ratio, indicated that HDES had higher preference in extracting molecular phenol from water, and the extraction was highly dependent on the availability of HDES to contact with the phenol solution. DES2 demonstrated a high phenol uptake capacity, and good stability at the tested operating temperature and phenol concentration ranges. Future studies could explore long-term stability and reusability of HDES, and examine the efficacy of HDES in removing other organic pollutants from water, broadening the scope of its application in water treatment.

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